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(54) Biocidal compositions for industrial materials.

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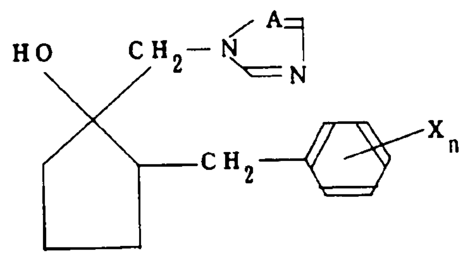
D scripti n

This invention relat s to the use of biocidal compositions for preventing deterioration of industrial materials.

2) Description of the R lated Art:

It has already been disclosed by the present inventors in GB 2180236 A that the compounds represented by the following formula (A) have plant disease controlling effects, plant growth controlling effects and herbicidal effects and can hence be used as agricultural and horticultural chemicals.



(A)

wherein X means a halogen atom or a C_1-C_5 alkyl, haloalkyl, phenyl, cyano or nitro group, n stands for 0 or an integer of 1-5, A denotes a nitrogen atom or CH, and when n is an integer of 2-5, Xs may be the same or different.

The present inventors also studied a group of azole derivatives including the compounds represented by the formula (A). As a result, it was found that in addition to the compounds represented by the formula (A), such azole derivatives also include those useful as agricultural and horticultural chemicals and further those not only capable of acting as an agricultural and horticultural chemical but also having effective antifungal activities in animals including human being [Japanese Patent Application Nos. 317754/1987 (corresponding to European Patent Application No. 88305090.8), 6054/1988 and 7822/1988].

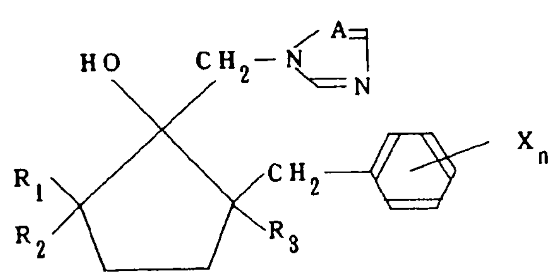
By the way, industrial materials, for example, natural materials such as paper, fibers, lumber and leather, synthetic materials such as paints and plastic materials, metal materials, inorganic materials and products formed of such materials are often contaminated by noxious microorganisms and deteriorated in quality. There has hence been a strong demand for the development of chemicals effective against microorganisms noxious to these industrial materials.

The present inventors have proceeded with a further investigation on the utility of the azole derivatives mentioned above. As a result, it has been found that a certain groups of azole derivatives have strong activities against microorganisms noxious to such industrial materials as referred to above, said microorganisms being totally different in field from microorganisms causing disease on agricultural and horticultural crops or fungi causing disease on human being and animals, leading to completion of this invention.

SUMMARY OF THE INVENTION

An object of this invention is to provide a method for preventing deterioration of industrial materials by using a biocidal composition effective against microorganisms which are noxious to industrial materials.

In one aspect of this invention, there is thus provided the use as a biocidal composition for an industrial material, of an azole derivative represented by the following formula (I):



(I)

wherein X means a halogen atom or a C_1-C_5 alkyl, haloalkyl, ph nyl, cyano or nitro group, n stands for 0 or an

integ r of 1-5, A denotes a nitrogen atom or CH, R_1 and R_2 mean individually a hydrogen atom or a C_1-C_5 alkyl group, R_3 denotes a hydrogen atom or a C_1-C_3 alkyl group, and when n is an integer of 2-5, Xs may be the same or differ nt.

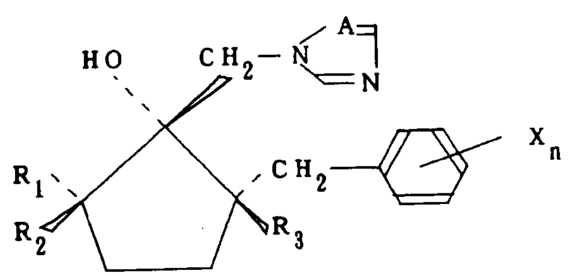
In another aspect of this invention, there is also provided a method for preventing deterioration of an industrial mat rial, which compris s applying to the industrial material a biocidally-effectiv amount of th azol derivative represented by the formula (I).

In the present invention, the azole derivative represented by the formula (I) has as its structural feature an azolylmethyl group at the 1-position of the cyclopentane ring, a substituted benzyl group or both a substituted benzyl group and a C_1-C_3 alkyl group at the 2-position, and a hydrogen atom or C_1-C_6 alkyl group at the 5-position. The above azole derivative useful in the practice of this invention therefore includes stereoisomers such as geometric isomers, i.e., cis-isomer and trans-isomer and optical isomers. This invention embraces not only single use of these isomers but also the use of mixtures containing individual isomers at desired ratios. In other words, it should be noted that the biocidal composition according to this invention contains these isomers either singly or in combination as active ingredient or ingredients. Since the above azole derivative contains a 1,2,4-triazole ring or imidazole ring, the azole derivative can be used in a form such as an acid addition salt with an inorganic acid or organic acid, a metal complex or the like.

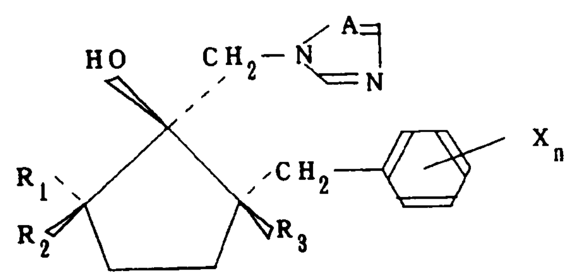
As will become apparent from results of tests to be described subsequently, the compound represented by the formula (I) exhibits strong activities against noxious microorganisms which contaminate industrial materials and cause their quality deterioration. When the biocidal composition according to this invention is applied, for example, to a natural material such as paper, fibers, lumber or leather, a synthetic material such as a paint coating, rubber or synthetic resin, a metallic material, inorganic material, or a product formed of the above-mentioned material, it can effectively prevent contamination or quality deterioration of such an industrial material.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

As illustrative examples of the azole derivative represented by the formula (I) and useful in the practice of this invention, may be mentioned compounds shown below in Table 1, in which the designated types of stereoisomers, namely, A type and B type mean those having the following structures respectively.



A type



B type

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: extending above the plane of the page

Table 1

Compound No.	Variables in formula (I)					Type of stereoisomer	Melting point (°C)
	R_1	R_2	R_3	Xn	A		
1	CH_3	CH_3	H	4-Cl	N	A	113-114
2	CH_3	CH_3	H	4-Cl	N	B	113-114
3	CH_3	CH_3	H	4-Cl	CH	A	133-134
4	CH_3	CH_3	H	4-Cl	CH	B	133-134
5	CH_3	CH_3	H	4-Br	N	A	129-130
6	CH_3	CH_3	H	4-Br	N	B	134-135
7	CH_3	CH_3	H	4-Br	CH	A	149-150
8	CH_3	CH_3	H	4-Br	CH	B	134-135
9	CH_3	CH_3	H	4-F	N	A	135-136
10	CH_3	CH_3	H	4-F	N	B	134-135
11	CH_3	CH_3	H	4-F	CH	A	131-133
12	CH_3	CH_3	H	4-F	CH	B	104-106
13	CH_3	CH_3	H	2,4-Cl_2	N	A	126-127
14	CH_3	CH_3	H	2,4-Cl_2	N	B	108-110
15	CH_3	CH_3	H	2,4-Cl_2	CH	A	131-132
16	CH_3	H	H	4-Cl	N	A	100-102
17	CH_3	H	H	4-Cl	CH	A	118-119
18	H	CH_3	H	4-Cl	N	A	75- 76
19	H	CH_3	H	4-Cl	N	B	79- 81

Table 1 (cont'd)

Compound No.	Variables in formula (I)					Type of stereoisomer	Melting point (°C)
	R_1	R_2	R_3	Xn	A		
20	CH_3	H	H	4-Cℓ	N	B	oily substance
21	CH_3	CH_3	H	H	N	A	oily substance
22	CH_3	CH_3	H	H	CH	A	128-130
23	CH_3	CH_3	H	4-CH_3	N	A	123-124
24	CH_3	CH_3	H	4-CH_3	N	B	114-115
25	CH_3	CH_3	H	4-CH_3	CH	A	132-133
26	CH_3	CH_3	H	4-CH_3	CH	B	130-131
27	CH_3	CH_3	H	2-F, 4-Cℓ	N	A	129-130
28	CH_3	CH_3	H	2-F, 4-Cℓ	CH	A	152-154
29	C_2H_5	H	H	4-Cℓ	N	A	82- 84
30	H	C_2H_5	H	4-Cℓ	N	A	93- 95
31	H	C_2H_5	H	4-Cℓ	N	B	76- 78
32	C_2H_5	H	H	4-Cℓ	N	B	110-112
33	C_2H_5	C_2H_5	H	4-Cℓ	N	A	124-126
34	C_2H_5	C_2H_5	H	4-Cℓ	N	B	143-145
35	C_2H_5	C_2H_5	H	4-Cℓ	CH	A	oily substance
36	C_2H_5	C_2H_5	H	4-Cℓ	CH	B	143-145
37	n-C_3H_7	H	H	4-Cℓ	N	A	83- 85

Table 1 (cont'd)

Compound No.	Variables in formula (I)					Type of stereoisomer	Melting point (°C)
	R_1	R_2	R_3	Xn	A		
38	H	n-C_3H_7	H	4-Cℓ	N	A	75- 77
39	n-C_3H_7	H	H	4-Cℓ	CH	A	115-117
40	C_2H_5	H	H	2,4-$Cℓ_2$	N	A	124-127
41	C_2H_5	H	H	2,4-$Cℓ_2$	CH	A	111-113
42	C_2H_5	H	H	4-F	N	A	73- 74
43	C_2H_5	H	H	4-F	CH	A	111-113
44	C_2H_5	H	H	4-Br	N	A	80- 82
45	C_2H_5	H	H	4-Br	CH	A	117-119
46	C_2H_5	H	H	4-C_6H_5	N	A	107-109
47	C_2H_5	H	H	4-C_6H_5	CH	A	169-170
48	C_2H_5	H	H	4-t-C_4H_9	N	A	oily substance
49	C_2H_5	H	H	4-t-C_4H_9	CH	A	132-133
50	i-C_3H_7	H	H	4-Cℓ	N	A	91- 92
51	n-C_5H_{11}	H	H	4-Cℓ	N	A	oily substance
52	n-C_5H_{11}	H	H	4-Cℓ	CH	A	92- 95
53	C_2H_5	H	H	4-Cℓ	CH	B	138-140
54	H	n-C_5H_{11}	H	4-Cℓ	N	A	oily substance
55	CH_3	CH_3	H	4-C_6H_5	N	A	122-124

Table 1 (cont'd)

Compound No.	Variables in formula (I)					Type of stereoisomer	Melting point (°C)
	R_1	R_2	R_3	Xn	A		
56	CH_3	CH_3	H	4-C_6H_5	N	B	116-118
57	CH_3	CH_3	H	4-C_6H_5	CH	A	162-163
58	CH_3	CH_3	H	4-C_6H_5	CH	B	165-167
59	i-C_3H_7	H	H	4-Cl	CH	A	oily substance
60	CH_3	CH_3	H	4-t-C_4H_9	N	A	107-108
61	CH_3	CH_3	H	4-t-C_4H_9	CH	A	167-168
62	H	i-C_3H_7	H	4-Cl	N	B	oily substance
63	H	i-C_3H_7	H	4-Cl	N	A	102-103
64	H	i-C_3H_7	H	4-Cl	CH	A	146-147
65	i-C_3H_7	H	H	4-Cl	N	B	120-121
66	n-C_4H_9	H	H	4-Cl	CH	A	oily substance
67	H	n-C_4H_9	H	4-Cl	N	A	94- 95
68	H	n-C_4H_9	H	4-Cl	N	B	oily substance
69	i-C_4H_9	H	H	4-Cl	N	A	oily substance
70	i-C_4H_9	H	H	4-Cl	CH	A	oily substance
71	n-C_4H_9	H	H	4-Cl	N	A	oily substance
72 Isomer a	CH_3	C_2H_5	H	4-Cl	N	A	72-a/72-b mixture 98-101
72 Isomer b	C_2H_5	CH_3	H	4-Cl	N	A	

Table 1 (cont'd)

Compound No.		Variables in formula (I)					Type of stereoisomer	Melting point (°C)
		R_1	R_2	R_3	Xn	A		
73	Isomer a	CH_3	C_2H_5	H	4-Cl	N	B	73-a/73-b mixture 117-119
	Isomer b	C_2H_5	CH_3	H	4-Cl	N	B	
74	Isomer a	CH_3	C_2H_5	H	4-Cl	CH	B	74-a/74-b mixture 122-127
	Isomer b	C_2H_5	CH_3	H	4-Cl	CH	B	
75		CH_3	CH_3	H	4-t-C_4H_9	N	B	oily substance
76		CH_3	CH_3	H	4-t-C_4H_9	CH	B	132-133
77		H	H	H	H	N	A	140-141
78		H	H	H	H	CH	A	130-131
79		H	H	H	4-CH_3	N	A	128-129
80		H	H	H	4-CH_3	CH	A	122-123
81		H	H	H	4-t-C_4H_9	N	A	129-130
82		H	H	H	4-t-C_4H_9	CH	A	123-124
83		H	H	H	2-Cl	N	A	154-155
84		H	H	H	2-Cl	CH	A	103-104
85		H	H	H	3-Cl	N	A	152-153
86		H	H	H	3-Cl	CH	A	105-106

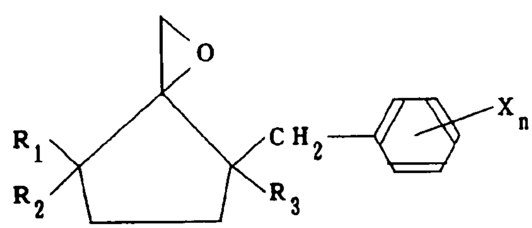
Table 1 (cont'd)

Compound No.	Variables in formula (I)					Type of stereoisomer	Melting point (°C)
	R_1	R_2	R_3	Xn	A		
87	H	H	H	4-Cℓ	N	A	115-116
88	H	H	H	4-Cℓ	CH	A	115-116
89	H	H	H	2,4-$Cℓ_2$	N	A	120-121
90	H	H	H	2,4-$Cℓ_2$	CH	A	150-151
91	H	H	H	4-F	N	A	135-136
92	H	H	H	4-F	CH	A	139-140
93	H	H	H	2,4-F_2	N	A	118-119
94	H	H	H	2,4-F_2	CH	A	144-145
95	H	H	H	2,6-F_2	N	A	104-105
96	H	H	H	2,6-F_2	CH	A	150-151
97	H	H	H	3,4-F_2	N	A	119-121
98	H	H	H	3,4-F_2	CH	A	103-105
99	H	H	H	2,3,4,5,6-F_5	N	A	118-120
100	H	H	H	3-CF_3	N	A	152-153
101	H	H	H	3-CF_3	CH	A	87- 88
102	H	H	H	2-F, 4-Cℓ	N	A	125-127
103	H	H	H	2-F, 4-Cℓ	CH	A	141-143
104	H	H	H	4-Br	N	A	106-107

Table 1 (cont'd)

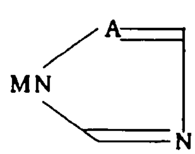
Compound No.	Variables in formula (I)					Type of stereoisomer	Melting point (°C)
	R_1	R_2	R_3	Xn	A		
105	H	H	H	4-Br	CH	A	119-120
106	H	H	H	$4-C_6H_5$	N	A	146-147
107	H	H	H	$4-C_6H_5$	CH	A	182-183
108	H	H	H	$4-NO_2$	N	A	131-132
109	H	H	H	4-CN	N	A	115-116
110	H	H	H	4-CN	CH	A	103-104
111	CH_3	CH_3	CH_3	4-Cℓ	N	A	159-160
112	CH_3	CH_3	CH_3	4-Cℓ	N	B	178-179
113	CH_3	CH_3	CH_3	4-Cℓ	CH	A	186-187
114	CH_3	CH_3	CH_3	4-Cℓ	CH	B	157-158

The azole derivatives useful in the practice of this invention can each be prepared by reacting an oxirane compound, which is represented by the following formula (II):



(II)

wherein X, R_1, R_2, R_3 and n have the same meanings as defined above, with a compound represented by the following formula (III):



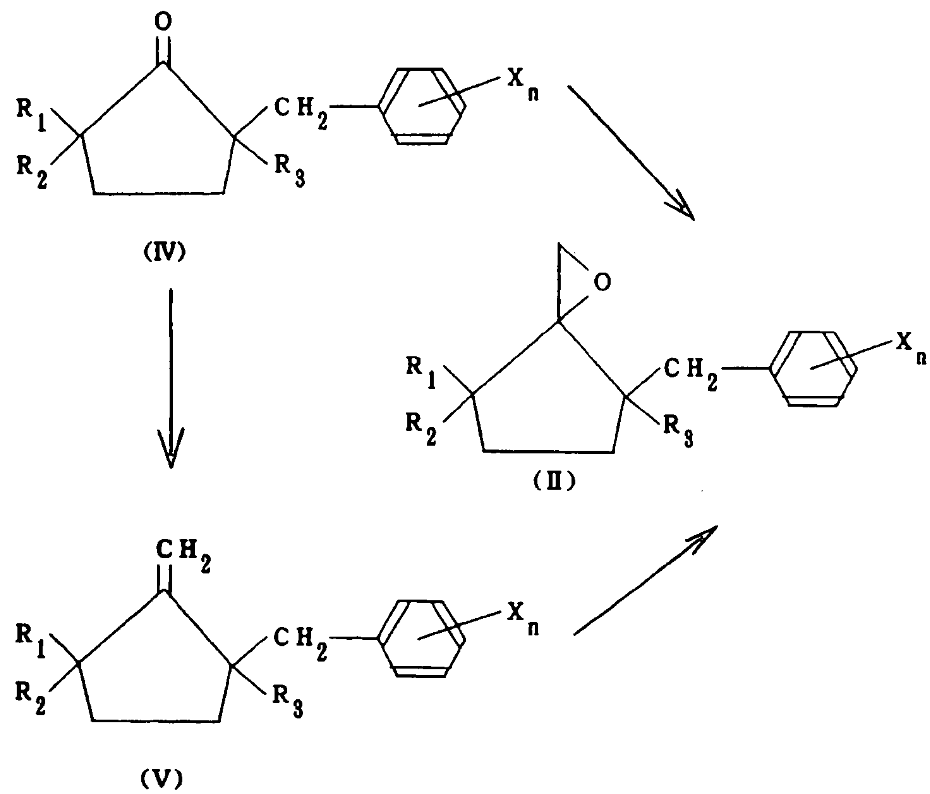
(III)

wherein M means a hydrogen atom or alkali metal and A has the sam m aning as defined abov , in the pres nce of a diluent.

Incid ntally, the oxirane compound represented by the formula (II) can be obtained by r acting a cyclopen-

tanone represented by formula (IV) below, for example, with dimethyloxosulfonium methylide or dimethylsulfonium methylide in the pr s nce of a diluent, for xample, in light of the process described in Organic Synthesis, 49, 78 (1968) and Journal of American Chemical Society, 1353 (1965).

Still more, as a differ nt method, there is a method by which a methylen cyclop ntane represented by th formula (V) is obtained from a cyclopentanon repr s nted by th formula (IV) through the Witting reaction [r fer to Org. Syn. 40, 66 (1966) and J. Org. Chem. 28, 1128 (1963)], and then the oxirane derivative represented by the formula (II) can be obtained from the thus prepared compound by the epoxidation [refer to Org. Syn. Coll. Vol., 4, 552 (1963) and Org. Syn., 49, 62 (1969)].



wherein X, R_1, R_2, R_3 and n have the same meanings as defined above.

The biocidal compositions for industrial materials, said compositions pertaining to the present invention, show controlling effects against microorganisms which grow on the industrial materials and cause deterioration of their base materials. Such microorganisms may include, for example, paper/pulp-deteriorating microorganisms including slime-forming microorganisms, such as Aspergillus sp., Trichoderma sp., Penicillium sp., Geotrichum sp., Chaetomium sp., Cadophora sp., Ceratostomella sp., Cladosporium sp., Corticium sp., Lentinus sp., Lezites sp., Phoma sp., Polysticus sp., Pullularia sp., Stereum sp., Trichosporium sp., Aerobacter sp., Bacillus sp., Desulfovibrio sp., Pseudomonas sp., Flavobacterium sp. and Micrococcus sp.; fibers-deteriorating microorganisms such as Aspergillus sp., Penicillium sp., Chaetomium sp., Myrothecium sp., Curvularia sp., Gliomastix sp., Memnoniella sp., Sarcopodium sp., Stachybotrys sp., Stemphylium sp., Zygorhynchus sp., Bacillus sp. and Staphylococcus sp.; lumber-deteriorating microorganisms such as Tyromyces palustris, Coriolus versicolor, Aspergillus sp., Penicillium sp., Rhizopus sp., Aureobasidium sp., Gliocladium sp., Cladosporium sp., Chaetomium sp. and Trichoderma sp.; leather-deteriorating microorganisms such as Aspergillus sp., Penicillium sp., Chaetomium sp., Cladosporium sp., Mucor sp., Paecilomyces sp., Pilobus sp., Pullularia sp., Trichosporon sp. and Tricothecium sp.; rubber/plastics-deteriorating microorganisms such as Aspergillus sp., Penicillium sp., Rhizopus sp., Trichoderma sp., Chaetomium sp., Myrothecium sp., Streptomyces sp., Pseudomonus sp., Bacillus sp., Micrococcus sp., Serratia sp., Margarinomyces sp. and Monascus sp.; paint-deteriorating microorganisms such as Aspergillus sp., Penicillium sp., Cladosporium sp., Aur obasidium sp., Gliocladium sp., Botryodiplodia sp., Macrosporium sp., Monilia sp., Phoma sp., Pullularia sp., Sporotrichum sp., Trichoderma sp., Bacillus sp., Prot us sp., Pseudomonas sp. and

Serratia sp.

Th biocidal compositions for industrial materials, said compositions pertaining to the present invention, can each be formulated by dissolving or dispersing an effectiv amount of the compound represented by th formula (I) in a suitable liquid v hicle or mixing it with a solid vehicle and optionally adding an mulsifi r, dis- p rsant, spr ading agent, p n trant, wetting agent, stabilizer and/or th like. One or more of other biocid s, insecticides, deterioration inhibitors and the like may also be incorporated.

Any liquid may be used as a liquid vehicle so long as it does not react with the effective ingredient. It is possible to use, for example, water, an alcohol such as methyl alcohol, ethyl alcohol, ethylene glycol or cellosolve, a ketone such as acetone or methyl ethyl ketone, an ether such as dimethyl ether, diethyl ether, dioxane or tetrahydrofuran, an aromatic hydrocarbon such as benzene, toluene, xylene or methylnaphthalene, an aliphatic hydrocarbon such as gasoline, kerosine, lamp oil, stove oil, furnace oil, machine oil or fuel oil, an acid amide such as dimethylformamide or N-methylpyrrolidone, a halogenated hydrocarbon such as chloroform or carbon tetrachloride, an ester such as ethyl acetate or the glycerin ester of a fatty acid, a nitrile such as acetonitrile, dimethylsulfoxide, or the like. As a solid vehicle on the other hand, it is possible to use fine particulate or granular material such as clay, kaolin clay, bentonite, acid clay, pyrophyllite, talc, diatomaceous earth, calcite, urea or ammonium sulfate. As an emulsifier or dispersant, it is possible to use a surfactant such as a soap, alkyl sulfonate, alkyl arylsulfonate, dialkyl sulfosuccinate, quaternary ammonium salt, oxyalkylamine, fatty acid ester, polyalkylene-oxide-type surfactant or anhydrosorbitol-type surfactant.

Upon formulation of the azole derivative of the formula (I) as an effective ingredient into a biocidal composition according to this invention, it is generally suitable to add it to give a concentration of 0.1-99.9 wt.% although its content may vary depending on the preparation form and application purpose of the biocidal composition.

In the present invention, a biocidally-effective amount of the azole derivative of the formula (I) can be applied in a preparation form, for example, as a wettable powder, dust, granules, paste, suspension or spray to an industrial material. The application to the industrial material can be effected, for example, by spraying or coating the surface of paper, pulp, fibers, lumber, leather, rubber product, synthetic resin product or coating. The biocidally-effective amount may be generally 0.005-5 wt.% or preferably 0.01-1 wt.%, both, based on an industrial material to be treated.

Examples

Preparation Example:

Preparation of a typical azole derivative of the formula (I) will hereinafter be described. It should however be noted that the other azole derivatives of the formula (I) can also be prepared likewise.

Preparation of 2-(4-chlorobenzyl)-2,5,5-trimethyl-1-(1H-1,2,4-triazol-1-ylmethyl)-1-cyclopentanol (Compound No. 111 in Table 1)

Anhydrous dimethylformamide (3 mℓ) was added with 230 mg of sodium hydride and further with 390 mg of 1H-1,2,4-triazole. The resultant mixture was stirred at room temperature until foaming subsided. The resulting solution was added with 2 mℓ of an anhydrous dimethylformamide solution which contained 1.0 g of 4-(4-chlorobenzyl)-4,7,7-trimethyl-1-oxaspiro[2.4]heptane, followed by stirring at 120°C for 24 hours. After allowing the thus-obtained reaction mixture to cool down, it was poured into ice water and then extracted with methylene chloride to obtain an organic layer. After washing the organic layer with aqueous saline solution, it was dried over anhydrous sodium sulfate, and the solvent was thereafter distilled off under reduced pressure. The thus-obtained residue was subjected to and purified by chromatography on a silica gel column (eluent: ethyl acetate). It was then recrystallized from n-hexane-ethyl acetate so that 1.06 g of the target compound was obtained.

By the way, the raw material,4-(4-chlorobenzyl)-4,7,7-trimethyl-1-oxaspiro[2.4]heptane, was obtained in the following manner.

2-(4-Chlorobenzyl)-2,5,5-trimethyl-1-methylene-cyclopentane (6.1 g) was dissolved in 60 mℓ of chloroform, followed by the addition of 8.5 g of m-chloroperbenzoic acid. The resultant mixture was stirred for 5 hours under ice cooling. Calcium hydroxide (4.0 g) was added, followed by stirring at room temperature for 30 minutes. A solid thus pr cipitat d was filter d off. From the chloroform lay r as th filtrate, chloroform was distilled off under reduced pressure to obtain a colorless oily substanc . The substance was subjected to and purified by chromatography on a silica g l column (eluent: 6:1 mixed solvent of n-h xan and methyl ne chloride), thereby obtaining 2.0 g of 4-(4-chlorobenzyl)-4,7,7-trimethyl-1-oxaspiro[2.4]heptane used in the above Preparation Exampl .

Biocidal Compositions and Tests:

The present invention will her inaft r be d scribed further by the following exemplary biocidal compositions and tests.

Composition 1:

A dust was obtained by grinding and mixing 1 wt.% of an invention compound (Compound No. 87), 89 wt.% of kaolin clay and 10 wt.% of talc.

Composition 2:

A wettable powder was obtained by grinding and mixing 25 wt.% of an invention compound (Compound No. 1), 2 wt.% of sodium ligninsulfonate, 2 wt.% of sodium lauryl sulfate and 71 wt.% of clay.

Test 1:

Each test compound according to this invention was added to a modified Mueller-Hinton culture medium (product of Nissui Seiyaku Kabushiki Kaisha) to give a predetermined concentration. The resultant culture medium was poured into Petri dishes and was caused to coagulate. They were inoculated with three kinds of noxious microorganisms (Staphylococcus sp., Bacillus sp. and Micrococcus sp.) respectively, followed by incubation at 37°C. Depending on whether those microorganisms had grown or not on the following day, the minimum inhibitory concentrations of the invention compound for the respective noxious microorganisms were determined. Based on the minimum inhibitory concentrations thus obtained, 5-stage ranking was conducted in accordance with the following system:

Minimum inhibitory concentration

1 .... at least 100 ppm
2 .... at least 50 ppm but lower than 100 ppm
3 .... at least 12.5 ppm but lower than 50 ppm
4 .... at least 3.13 ppm but lower than 12.5 ppm
5 .... lower than 3.13 ppm

Table 2

Sample compound (No. in Table 1)	Test microorganism		
	S.sp.	B.sp.	M.sp.
1	2	3	3
3	2	3	5
4	2	3	5
5	2	3	4
6	2	2	3
7	3	3	4
8	2	2	4
9	1	2	3
10	1	2	2
11	1	3	5
12	1	3	4
13	3	3	4
14	3	3	4
16	2	2	3
17	2	3	4
19	2	1	2
23	1	2	3
24	2	2	3
25	2	3	4
26	2	3	4
27	2	3	3
28	3	4	5
29	2	2	3
30	2	2	4
31	2	2	2
32	3	2	3
34	3	3	4
36	4	5	5
37	3	3	4
38	3	3	4
39	3	4	5
40	3	3	4
41	4	5	5
42	1	2	2
43	1	3	4
44	3	3	3
45	3	4	5

Table 2 (cont'd)

Sample compound (No. in Table 1)	Test microorganism		
	S.sp.	B.sp.	M.sp.
47	4	5	5
48	3	3	4
49	4	4	5
50	3	3	4
51	4	3	4
52	4	4	5
53	2	1	2
54	4	4	4
55	3	3	4
56	3	3	4
57	3	4	5
58	4	4	5
59	3	4	5
60	3	4	4
61	3	4	5
62	3	2	3
63	3	2	4
64	3	3	5
65	3	3	4
66	4	3	5

Saple compound (No. in Table 1)	Test microorganism		
	S.sp.	B.sp.	M.sp.
67	3	3	5
68	3	2	4
69	3	3	4
70	3	3	5
71	4	3	4
75	3	3	4
76	3	4	4
78	1	1	3
80	1	2	3
81	1	3	3
82	3	3	5
84	1	2	3
86	1	3	4
90	3	4	5
92	1	2	3
94	1	2	3

Table 2 (cont'd)

Sample compound (No. in Table 1)	Test microorganism		
	S.sp.	B.sp.	M.sp.
96	1	2	3
98	1	2	4
101	1	3	4
103	2	3	4
104	1	1	3
105	2	3	4
107	1	3	5

The abbreviation in Table 2 shows each of the following microorganisms:

S.sp.; Staphylococcus sp.
B.sp.; Bacillus sp.
M.sp.; Micrococcus sp.

Test 2:

Each test compound according to this invention was added to a potato-sucrose-agar culture medium to give 100 ppm. The resultant culture medium was poured into Petri dishes and was caused to coagulate. They were inoculated with seven kinds of noxious microorganisms (Aspergillus niger, Aspergillus terreus, Aureobasidium pullulans, Rhizopus stolonifer, Penicillium citrinum, Penicillium funiculosum and Chaetomium globosum) respectively, followed by incubation at 28°C for 7 days. Hyphae elongation inhibitory rates (%) were determined respectively in accordance with the below-described equation. Based on the hyphae elongation inhibitory rates, the test results were ranked in four stages by the following ranking system. The results are shown in Table 3.

$$\text{Hyphae elongation inhibitory rate, \%} = \frac{\text{Hyphae elongation in non-treated group, mm} - \text{Hyphae elongation in treated group group, mm}}{\text{Hyphae elongation in non-treated group, mm}} \times 100$$

Ranking system:

<u>Hyphae elongation inhibitory rate, %</u>

1 .... at least 0% but smaller than 25%
2 .... at least 25% but smaller than 50%
3 .... at least 50% but smaller than 75%
4 .... at least 75% and up to 100%

Table 3

Sample compound (No. in Table 1)	Test microorganism						
	Asp.t.	Asp.n.	Aur.p.	Rhi.s.	Pen.c.	Pen.f.	Chae.g.
1	4	4	4	4	4	4	4
2	4	4	4	4	2	4	4
3	4	4	4	4	4	4	4
4	4	4	4	4	4	4	4
5	4	4	4	4	4	4	4
6	4	4	4	4	2	4	4
7	4	4	4	4	4	4	4
8	4	4	4	4	4	4	4
9	4	4	4	4	4	4	4
10	4	4	4	4	1	4	4
11	4	4	4	4	4	4	4
12	4	4	4	4	4	4	4
13	4	4	4	4	2	4	4
14	2	4	4	4	2	4	4
19	4	4	4	4	2	4	4
20	4	4	4	4	4	4	4
21	4	4	4	4	4	4	4
22	4	4	4	4	4	4	4
23	4	4	4	4	4	4	4

Table 3 (Cont'd)

Sample compound (No. in Table 1)	Test microorganism						
	Asp.t.	Asp.n.	Aur.p.	Rhi.s.	Pen.c.	Pen.f.	Chae.g.
24	4	4	4	4	2	4	4
25	4	4	4	4	4	4	4
26	4	4	4	4	4	4	4
27	4	4	4	4	4	4	4
28	4	4	4	4	4	4	4
29	4	4	4	4	4	4	4
30	4	4	4	4	4	4	4
31	4	4	4	4	4	4	4
32	4	4	4	4	4	4	4
33	4	4	4	4	4	4	4
34	4	4	4	4	4	4	4
35	4	4	4	4	4	4	4
36	4	4	4	4	4	4	4
37	4	4	4	4	4	4	4
38	4	4	4	4	4	4	4
39	4	4	4	4	4	4	4
40	1	4	4	4	4	4	4
41	4	4	4	4	4	4	4
42	4	4	4	4	4	4	4

Table 3 (Cont'd)

Sample compound (No. in Table 1)	Test microorganism						
	Asp.t.	Asp.n.	Aur.p.	Rhi.s.	Pen.c.	Pen.f.	Chae.g.
43	4	4	4	4	4	4	4
44	4	4	4	4	4	4	4
45	4	4	4	4	4	4	4
46	2	4	1	1	4	1	4
47	4	4	1	1	4	4	4
48	1	4	4	3	2	1	4
49	4	4	4	4	4	4	4
50	4	4	4	4	4	4	4
51	4	4	4	4	4	4	4
52	4	4	4	4	4	4	4
53	4	4	4	4	4	4	4
54	4	4	4	4	4	3	4
55	4	4	4	3	4	1	4
56	2	3	4	3	2	2	4
57	4	4	1	1	4	4	4
58	4	4	4	4	4	4	4
59	4	4	4	4	4	4	4
60	2	3	3	1	2	1	4
61	4	4	4	1	4	2	4

Table 3 (Cont'd)

Sample compound (No. in Table 1)	Test microorganism						
	Asp.t.	Asp.n.	Aur.p.	Rhi.s.	Pen.c.	Pen.f.	Chae.g.
63	4	4	4	4	4	4	4
64	4	4	4	4	4	4	4
66	4	4	4	4	4	4	4
67	4	4	4	4	4	4	4
68	2	3	4	3	2	1	4
69	4	4	4	4	4	3	4
70	4	4	4	4	4	4	4
71	4	4	4	4	4	4	4
75	1	2	3	1	1	2	4
76	4	4	4	4	4	4	4
77	2	4	4	1	1	2	4
78	4	4	1	1	3	4	4
79	4	4	4	1	3	3	4
80	4	4	4	4	4	3	4
81	1	3	4	1	3	1	4
82	1	4	1	1	4	1	4
84	1	4	4	1	2	3	4
85	4	4	1	1	4	2	4
86	4	4	2	1	4	4	4

Table 3 (Cont'd)

Sample compound (No. in Table 1)	Test microorganism						
	Asp.t.	Asp.n.	Aur.p.	Rhi.s.	Pen.c.	Pen.f.	Chae.g.
87	4	4	4	4	4	4	4
88	4	4	4	4	4	4	4
89	1	4	4	4	2	4	4
90	4	4	4	4	4	4	4
91	2	4	4	4	1	2	4
92	4	4	1	4	4	4	4
94	1	4	1	1	2	3	4
96	3	4	4	1	2	2	4
97	4	4	4	4	3	3	4
98	4	4	1	1	4	4	4
99	1	4	4	4	1	1	4
101	4	4	4	1	4	2	4
102	2	4	4	4	2	4	4
103	4	4	4	4	4	4	4
104	4	4	4	4	4	4	4
105	4	4	4	4	4	4	4
106	1	4	1	1	4	2	4
107	4	4	4	1	4	4	4
109	2	4	4	1	1	1	4

Table 3 (Cont'd)

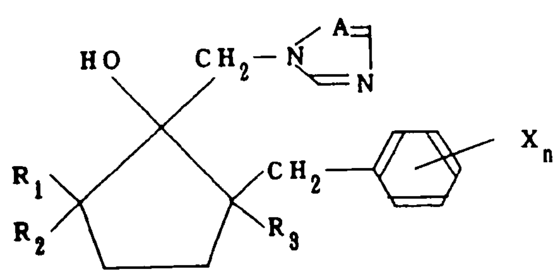
Sample compound (No. in Table 1)	Test microorganism						
	Asp.t.	Asp.n.	Aur.p.	Rhi.s.	Pen.c.	Pen.f.	Chae.g.
111	4	4	4	4	4	4	4
112	1	4	4	1	1	1	4
113	4	4	4	4	4	4	4
114	4	4	4	4	4	4	4

The abbreviation in Table 3 shows each of the following microorganisms:

Asp.t.; *Aspergillus terreus*
Asp.n.; *Aspergillus niger*
Aur.p.; *Aureobasidium pullulans*
Rhi.s.; *Rhizopus stolonifer*
Pen.c.; *Penicillium citrinum*
Pen.f.; *Penicillium funiculosum*
Chae.g.; *Chaetomium globosum*

Claims

1. Use of an azole derivative represented by the following formula (I):

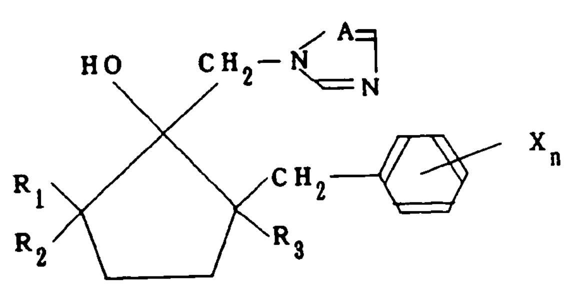


(I)

wherein X means a halogen atom or a C_1-C_5 alkyl, haloalkyl, phenyl, cyano or nitro group, n stands for 0 or an integer of 1-5, A denotes a nitrogen atom or CH, R_1 and R_2 mean individually a hydrogen atom or a C_1-C_6 alkyl group, R_3 denotes a hydrogen atom or a C_1-C_3 alkyl group, and when n is an integer of 2-5, Xs may be the same or different, as a biocide in an industrial material.

2. Use as claimed in Claim 1, wherein the industrial material is selected from paper, pulp, fibers, lumber, leather, rubber, synthetic resins and paints.

3. A method for preventing deterioration of an industrial material, which comprises applying to the industrial material a biocidally-effective amount of an azole derivative represented by the following formula (I):



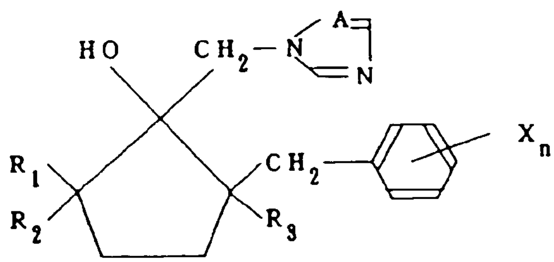
(I)

wherein X means a halogen atom or a C_1-C_5 alkyl, haloalkyl, phenyl, cyano or nitro group, n stands for 0 or an integer of 1-5, A denotes a nitrogen atom or CH, R_1 and R_2 mean individually a hydrog n atom or a C_1-C_5 alkyl ,group, R_3 denotes a hydrogen atom or a C_1-C_3 alkyl group, and when n is an integer of 2-5, Xs may b the same or different.

4. The method as claimed in Claim 3, wher in the industrial material is sel cted from paper, pulp, fibers, lumber, leather, rubber, synthetic resins and paints.

Patentansprüche

1. Verwendung eines Azolderivats der folgenden Formel (I)

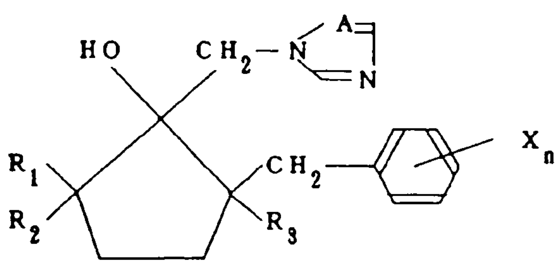


(I)

worin X ein Halogenatom oder eine C_1-C_5-Alkyl-, Halogenalkyl-, Phenyl-, Cyano- oder Nitrogruppe bedeutet, n für 0 oder eine ganze Zahl von 1 bis 5 steht, A ein Stickstoffatom oder CH darstellt, R_1 und R_2 individuell ein Wasserstoffatom oder eine C_1-C_5-Alkylgruppe bedeuten, R_3 ein Wasserstoffatom oder eine C_1-C_3-Alkylgruppe ist und, wenn n eine ganze Zahl von 2 bis 5 ist, die Reste X gleich oder unterschiedlich sein können; als Biozid in einem industriellen Material.

2. Verwendung nach Anspruch 1, worin das industrielle Material ausgewählt ist unter Papier, Zellstoff, Fasern, Holz, Leder, Gummi, kunstharzen und Lacken.

3. Methode zum Verhindern der Schädigung eines industriellen Materials, bei dem auf das industrielle Material eine biozid-wirksame Menge eines Azolderivats der folgenden Formel (I) aufgetragen wird:



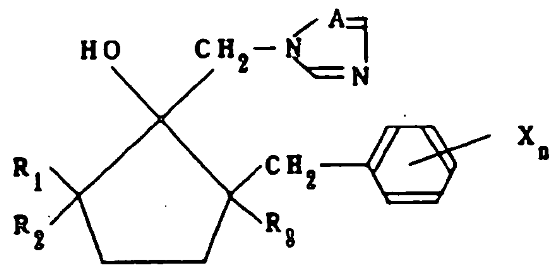
(I)

worin X ein Halogenatom oder eine C_1-C_5-Alkyl-, Halogenalkyl-, Phenyl-, Cyano- oder Nitrogruppe bedeutet, n für 0 oder eine ganze Zahl von 1 bis 5 steht, A ein Stickstoffatom oder CH darstellt, R_1 und R_2 individuell ein Wasserstoffatom oder eine C_1-C_5-Alkylgruppe bedeuten, R_3 ein Wasserstoffatom oder eine C_1-C_3-Alkylgruppe ist und, wenn n eine ganze Zahl von 2 bis 5 ist, die Reste X gleich oder unterschiedlich sein können.

2. Methode nach Anspruch 3, worin das industrielle Material ausgewählt ist unter Papier, Zellstoff, Fasern, Holz, Leder, Gummi, kunstharzen und Lacken.

Revendications

1. Utilization d'un dérivé d'azole représenté par la formule suivante (I):

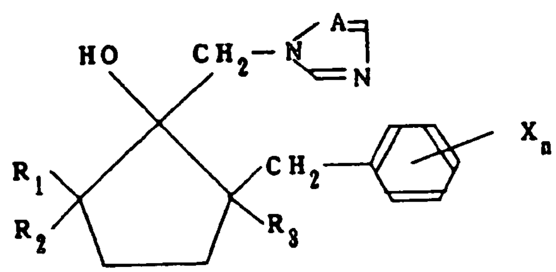


(I)

dans laquelle X rprésente un atome d'halogène ou un groupe alkyle en C_{1-5} haloalkyle, phényle, cyano ou nitro, n est 0 ou un entier de 1-5, A représente un atome d'azote ou un radical CH, R_1 et R_2 représente chacun un atome d'hydrogène ou un groupe alkyle en C_{1-5}, R_3 représente un atome d'hydrogène ou un groupe alkyle en C_{1-3}, et lorsque n est un entier de 2-5, les X peuvent être identiques ou différents, en tant que biocide dans un matériau industriel.

2. Utilisation suivant la revendication 1, dans laquelle le matériau industriel est choisi parmi le papier, la pulpe, les fibres, le bois de charpente, le cuir, le caoutchouc, les résines de synthèse et les peintures.

3. Procédé pour empêcher la détérioration d'un matériau industriel, qui comprend l'application sur ce matériau industriel d'une quantité active en tant que biocide, d'un dérivé d'azole représenté par la formule suivante (I):



(I)

dans laquelle X représente un atome d'halogène ou un groupe alkyle en C_{1-5}, haloalkyle, phényle, cyano ou nitro, n est 0 ou un entier de 1-5, A représente un atome d'azote ou un radical CH, R_1 et R_2 représentent chacun un atome d'hydrogène ou un groupe alkyle en C_{1-5}, R_3 représente un atome d'hydrogène ou un groupe alkyle en C_{1-3}, et lorsque n est un entier de 2-5, les X peuvent être identiques ou différents.

4. Procédé suivant la revendication 3, dans lequel le matériau industriel est choisi parmi le papier, la pulpe, les fibres, le bois de charpente, le cuir, le caoutchouc, les résines de synthèse et les peintures.